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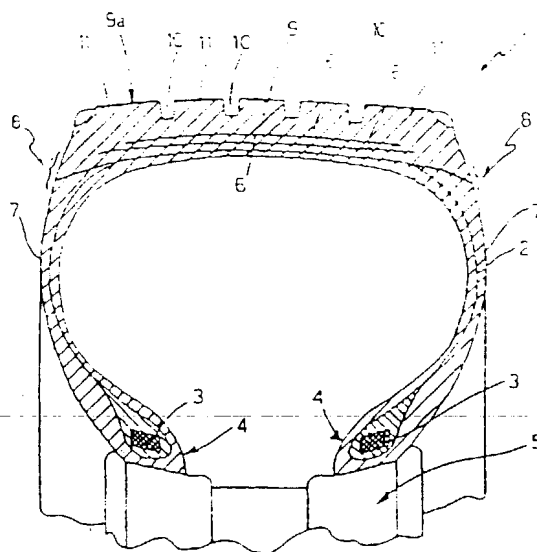
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- (54) Title: TIRE COMPRISING A HYDROPHILIC POLYMER AND ELASTOMERIC COMPOSITION EMPLOYED THEREIN



- (57) **Abstract:** A tire for vehicle wheels comprising at least one element made of a cross-linked elastomeric material including a hydrophilic polymer, and an elastomeric composition comprising a hydrophilic polymer employed therein. Preferably, said element is a tread belt. The composition comprises: at least one elastomeric diene polymer; at least one thermoplastic polymer having a main hydrocarbon chain to which hydrophilic groups are linked; at least one polymer containing functional groups reactive with said hydrophilic groups. The hydrophilic polymer is capable of absorbing significant amounts of water, without however dissolving and thus being easily removed from the elastomeric matrix. Besides, the hydrophilic polymer may carry out a reinforcing action of the elastomeric material and may therefore at least partly replace the conventional reinforcing fillers.

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TIRE COMPRISING A HYDROPHILIC POLYMER AND ELASTOMERIC  
COMPOSITION EMPLOYED THEREIN

DESCRIPTION

The present invention relates to a tire for vehicle  
5 wheels and to an elastomeric composition. More  
particularly, the present invention relates to a tire for  
vehicle wheels comprising at least one element made of a  
cross-linked elastomeric material including a hydrophilic  
polymer, and to an elastomeric composition comprising a  
10 hydrophilic polymer.

In the rubber industry, in particular in the  
manufacture of tires for vehicle wheels, the use is known  
of elastomeric compositions wherein reinforcing fillers  
have been incorporated in the polymer base, in order to  
15 improve the characteristics of the cross-linked product, in  
particular mechanical properties and abrasion resistance.  
Thanks to its high reinforcing efficiency, carbon black is  
the most widely employed reinforcing filler. However,  
carbon black imparts to the cross-linked product marked  
20 hysteretic characteristics, i.e. an increase of heat  
dissipated in dynamic conditions, which, as is known,  
causes, in the case of a tire, an increase in the rolling  
resistance of the tire itself. This leads to an increase of  
the fuel consumption of the vehicles, and hence of both  
25 locomotion costs and air pollution. It is possible to try  
to reduce such adverse effects by employing smaller amounts  
of carbon black and/or a carbon black having a smaller  
surface area. This inevitably leads to a reduction of the  
reinforcing action, with a worsening of the mechanical  
30 properties and of the abrasion resistance of the final  
product.

In order to reduce the hysteretic characteristics of  
the cross-linked products it is known to use the so-called

"white" reinforcing fillers, such as gypsum, talc, kaolin, bentonite, titanium dioxide, silicates of various types and especially silica, which replaces carbon black either entirely or partly. In this regard, see for example  
5 European patent EP-501,227.

The use of silica-based reinforcing fillers involves several drawbacks, substantially related to the poor affinity of the same with respect to the elastomers commonly used in the tire manufacture. In particular, to  
10 obtain a good dispersion degree of silica within the polymer matrix it is necessary to submit the elastomeric compositions to an extensive thermal-mechanical mixing action. To increase the affinity between silica and the elastomeric matrix, it is necessary to employ suitable  
15 coupling agents, for instance sulfur-containing organosilane products. However, the need of using such coupling agents sets a limit to the maximum temperature that can be reached during mixing and thermal-mechanical processing operations, on pain of an irreversible thermal  
20 degradation of the coupling agent.

Therefore, it is still strongly felt the need of introducing in the rubber compositions for tires new fillers which impart to the end product performances at least comparable to those obtained with conventional  
25 fillers, but without showing the drawbacks mentioned hereinabove. Said fillers should also be able to modulate the performances of the finished product as a function of use conditions.

In the prior art, it was for instance suggested to  
30 introduce hydrophilic polymers in elastomeric compositions, particularly in the rubber compositions used for the manufacture of tire treads, in order to increase the road grip of the tire, in particular on wet or iced grounds.

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For instance, in Japanese patent application (Kokai) JP-H5-170976 a tire is described which has an improved road grip on ice or snow grounds, wherein the tread includes short fibers and from 1 to 15 phr of powdered polyvinylalcohol (phr = parts by weight per 100 parts by weight of rubber). The fibers, for instance cellulose or synthetic polymer fibers, are oriented along the circumferential direction of the tire, so as to impart anisotropic characteristics. Road grip on ice or snow surfaces is improved by the presence of polyvinylalcohol particles which, when contacted with water, dissolve, leaving in the tread cavities which increase roughness and hence road grip of the tread. The amount of polyvinyl alcohol powder should not exceed 15 phr, so as not to worsen wear resistance to an unacceptable extent. Besides, low amounts of polyvinylalcohol are necessary not to increase tread stiffness and therefore not to worsen the road grip on dry grounds.

In European patent application EP-896,981, an elastomeric composition for use in tire tread manufacture is described, which includes modified polyvinylalcohol, in the form of powder or fibers. Such modified polyvinylalcohol has polyoxyalkylene groups along the chain, which increase the water solubility of the polymer, hence promoting dissolution of the same when the tread gets in touch with a wet surface, leaving cavities in the tread itself and forming a sticky layer at the interface with the road surface which should increase the tire road grip.

The use of hydrophilic polymers deriving from starch in elastomeric compositions is described in US patents 5,374,671 and 5,545,680. In particular, such patents describe elastomeric compositions comprising from 1 to 50 phr of a hydrophilic polymer having a glass transition temperature ( $T_g$ ) ranging from 150°C to 0°C depending upon the absorbed amount of water. Such hydrophilic polymer is a

destructured starch comprising amylose, amylopectine, or mixtures thereof. The presence of the destructured starch in a rubber composition for tire treads is said to increase traction on wet grounds, while reducing at the same time rolling resistance on dry roads. The destructured starch may be homogeneously dispersed throughout the elastomeric matrix or, preferably, it is immiscible with the polymeric matrix so that it tends to form fibers, preferably oriented fibers, within said matrix. Since destructured starch is a hydrolyzable and biodegradable polymer, its presence in a tire is said to increase its biodegradability. A grafting agent may be added to the rubber composition, in order to bind the hydrophilic polymer to the elastomeric base. No indications are given either about the grafting agent to be used, or on how to accomplish such grafting.

US patent 5,672,639 describes an elastomeric composition reinforced with a destructured starch combined with a plasticizer compatible with the destructured starch, so as to form a starch/plasticizer composite. With respect to destructured starch as such, said composite is said to have a better miscibility in the elastomeric matrix and would therefore prevent the formation of agglomerates of non dispersed starch. The plasticizer has a softening point lower than the softening point of destructured starch. In particular, poly(ethylene-vinylalcohol) having a softening point lower than 160°C, preferably comprised between 90° and 130°C, may be employed as a plasticizer. Other products which may be used as plasticizers include: ethylene/vinylacetate copolymers, ethylene/glycidylacrylate copolymers and ethylene/maleic anhydride copolymers, cellulose acetate, diesters of dibasic organic acids, and the like. To try to couple the starch/plasticizer composite with the elastomeric matrix, the addition of a coupling agent having a group which reacts with the hydroxyl groups of the composite, and a group capable of interacting with

the elastomeric matrix is suggested. To this aim, the use of coupling agents normally employed in silica-containing rubber compositions, in particular an organosilane tetrasulfide, is indicated.

5 In the Applicant's perception, the elastomeric compositions including a hydrophilic polymer should satisfy various requirements to render their use actually advantageous in the manufacture of cross-linked products, and in particular tires. First of all, such compositions,  
10 once cross-linked, should be able to absorb significant amounts of water, so as to change the performance of the product when the latter gets in touch with water. On the other hand, the presence of the hydrophilic polymer should not jeopardize the basic characteristics of the elastomeric  
15 cross-linked composition, e.g. tensile properties (in particular, tensile stress at break, elongation at break and modulus), dynamic properties (in particular, dynamic modulus and tandelta), and abrasion resistance.

The Applicant has now found that it is possible to  
20 address the above requirements by introducing in the elastomeric matrix a thermoplastic polymer containing hydrophilic groups as defined hereinafter, combined with a polymer having groups reactive with said hydrophilic groups. In this way, it is possible to produce an article  
25 wherein the hydrophilic polymer is capable of absorbing significant amounts of water without dissolving and, therefore, being easily removed from the elastomeric matrix. Besides, the hydrophilic polymer is able to exert a reinforcing  
30 ~~reinforcing action on the elastomeric material, thus~~ replacing, at least partially, the conventional reinforcing fillers, while keeping excellent, both tensile and dynamic, mechanical properties.

In a first aspect, the present invention therefore relates to a tire for vehicle wheels comprising at least

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one element made of an elastomeric material, characterized in that said element includes a composition comprising:

- (a) at least one elastomeric diene polymer;
- (b) at least one thermoplastic polymer having a main hydrocarbon chain to which hydrophilic groups are linked;
- (c) at least one polymer containing functional groups reactive with said hydrophilic groups.

In a preferred aspect, said element including said composition is a tread belt.

In another aspect, the present invention relates to an elastomeric composition comprising:

- (a) at least one elastomeric diene polymer;
- (b) at least one thermoplastic polymer having a main hydrocarbon chain to which hydrophilic groups are linked;
- (c) at least one polymer containing functional groups reactive with said hydrophilic groups.

In the present description and claims, by the expression "thermoplastic polymer having a main hydrocarbon chain to which hydrophilic groups are linked" (for the sake of brevity also "hydrophilic polymer") it is meant a synthetic polymer wherein hydrophilic groups, either directly or through side groups, are linked to the main hydrocarbon chain, either linear or branched, and free from glycoside bonds. As known, glycoside bonds are ether bonds, cleavable by hydrolysis, deriving from polycondensation of monosaccharides, which are typically present in polysaccharides such as starch and cellulose.

In the present description and claims, by "hydrophilic groups" it is meant groups which are able to bind water molecules by means of hydrogen bonds.

According to a preferred embodiment, the hydrophilic polymer is present in the elastomeric composition in a quantity comprised between 0.1 and 100 phr, preferably



between 3 and 50 phr, even more preferably between 5 and 20 phr. As is known, "phr" means parts by weight per 100 parts by weight of elastomeric base.

Preferably, the polymer containing functional groups  
5 reactive with the hydrophilic groups (in the following also referred to, for the sake of brevity, "functionalized polymer") is present in the elastomeric composition in a quantity so as to obtain a weight ratio between the hydrophilic polymer and the functionalized polymer  
10 comprised between 0.5:1 and 10:1, preferably between 1:1 and 5:1.

According to a preferred embodiment, said hydrophilic groups are selected from:

hydroxyl groups -OH;  
15 carboxylic groups -COOH, possibly at least partially in the salt form;  
ester groups -COOR (R = alkyl or hydroxyalkyl);  
amide groups -CONH<sub>2</sub>;  
sulfonic groups -SO<sub>3</sub>H, possibly at least partially in  
20 the salt form.

Preferably, the hydrophilic polymers according to the present invention are capable to absorb at least 0.1% by weight of water based on the polymer weight, after a 24-hour exposure in an environment having a 50% relative  
25 humidity at the temperature of 24°C (according to standard method ASTM D570).

Preferably, the hydrophilic polymers according to the present invention are thermoplastic products having a melting temperature lower than 230°C, preferably comprised  
30 between 200° and 130°C.

The hydrophilic polymers according to the present invention may be selected in particular from: polyacrylic acid, polymethacrylic acid, polyhydroxyalkylacrylate,

polyalkylacrylate, polyacrylamide, acrylamide/acrylic acid  
copolymers, polyvinylalcohol, polyvinylacetate,  
vinylalcohol/vinylacetate copolymers, ethylene/vinylacetate  
copolymers, ethylene/vinylalcohol copolymers,  
5 ethylene/vinylalcohol/vinylacetate terpolymers, polyvinyl-  
sulfonic acid, polystyrene sulfonate, and mixtures thereof.

According to a particularly preferred embodiment, said  
hydrophilic polymer comprises repeating units having the  
formula



10

with a random or block distribution along the chain.

This preferred class of hydrophilic polymers  
encompasses: polyvinylalcohol, ethylene/vinylalcohol  
copolymers, ethylene/vinylalcohol/vinylacetate terpolymers.  
15 Polymers may also be used wherein the groups of formula (I)  
have been at least partially modified, for instance by  
partial acetylation with aliphatic aldehydes (as described,  
for instance, in US patent 4,002,796).

The following are particularly preferred:

20 (i) vinylalcohol polymers obtained by hydrolysis of  
polyvinylacetate, with a hydrolysis degree comprised  
between 50 and 100 mol %, preferably between 70 and 90 mol  
%;

(ii) ethylene/vinylalcohol copolymers having a content  
25 of ethylene units generally comprised between 20 and 60 mol  
%, preferably between 25 and 50 mol %.

Copolymers of type (i) are commercially available  
under the trademarks Mowiol® (Clariant), Gohsenol® (Nippon  
Gohsei), Elvanol® (Du Pont), Airvol® (Air Products).  
30 Copolymers of type (ii) are commercially available under

the trademark Soarnol® (Atochem).

The polymer containing functional groups reactive with the hydrophilic groups employable in the present invention is generally a thermoplastic hydrocarbon polymer in which functional groups have been introduced selected from: carboxylic groups, anhydride groups, ester groups, silane groups, epoxy groups. The amount of functional groups present in the polymer is generally comprised between 0.05 and 50 parts by weight, preferably between 0.1 and 10 parts by weight, based on 100 parts by weight of the polymer.

The functional groups may be introduced during the production of the polymer, by co-polymerization with corresponding functionalized monomers containing at least one ethylene unsaturation, or by subsequent modification of the hydrocarbon polymer by grafting said functionalized monomers in the presence of a free radical initiator (in particular, an organic peroxide).

Alternatively, it is possible to introduce the functional groups by reacting pre-existing groups of the hydrocarbon polymer with a suitable reagent, for instance by an epoxydation reaction of a diene polymer containing double bonds along the main chain and/or as side groups with a peracid (for instance, m-chloroperbenzoic acid or peracetic acid) or with hydrogen peroxide in the presence of a carboxylic acid or a derivative thereof.

In particular, the base hydrocarbon polymer may be selected from:

(a) ethylene homopolymers or copolymers of ethylene with an alpha-olefin having from 3 to 12 carbon atoms (preferably propylene or 1-octene), comprising in general from 35 to 97 mol % of ethylene and from 3 to 65 mol % of alpha-olefin,

(b) propylene homopolymers or copolymers of propylene

with ethylene and/or an alpha-olefin having from 4 to 12 carbon atoms (preferably 1-butene), the total amount of ethylene and/or alpha-olefin being less than 10 mol %;

5 (c) polymers of conjugated diene monomers having from 4 to 12 carbon atoms (preferably 1,3-butadiene, isoprene or mixtures thereof), possibly copolymerized with a monovinylarene having from 8 to 20 carbon atoms (preferably styrene) in an amount not higher than 50% by weight;

10 (d) homopolymers of monovinylarenes (in particular styrene) or copolymers thereof with ethylene.

Functionalized monomers which may be used include for instance: silanes containing at least one ethylene unsaturation; epoxy compounds containing at least one ethylene unsaturation; monocarboxylic or, preferably, 15 dicarboxylic acids containing at least one ethylene unsaturation, or derivatives thereof in particular anhydrides or esters.

Examples of silanes containing at least one ethylene unsaturation are: gamma-methacryloxypropyltrimethoxy- 20 silane, allyltrimethoxy-silane, allyltriethoxy-silane, allylmethyldimethoxy-silane, allylmethyldiethoxy-silane, vinyltris(2-methoxyethoxy)-silane, vinyltrimethoxy-silane, vinylmethyldimethoxy-silane, vinyltriethoxy-silane, and the like, or mixtures thereof.

25 Examples of epoxy compounds containing at least one ethylene unsaturation are: glycidyl acrylate, glycidyl methacrylate, itaconic acid monoglycidyl ester, maleic acid glycidylester, vinylglycidyl ether, allylglycidyl ether, and the like, or mixtures thereof.

30 Examples of monocarboxylic or dicarboxylic acids containing at least one ethylene unsaturation are: maleic acid, maleic anhydride, fumaric acid, citraconic acid, itaconic acid, acrylic acid, methacrylic acid, and the

like, and anhydrides or esters derived therefrom, or mixtures thereof. Maleic anhydride is particularly preferred.

Polyolefins grafted with maleic anhydride are  
5 available as commercial products identified for instance by the trademarks Fusabond® (Du Pont), Orevac® (Elf Atochem), Exxelor® (Exxon Chemical), Yparex® (DSM).

The elastomeric diene polymers usable as polymeric  
base in the present invention may be selected from those  
10 commonly used in sulfur-vulcanizable elastomeric compositions, particularly suitable for tire manufacture, i.e. among unsaturated chain elastomeric polymers or copolymers having a glass transition temperature generally lower than 20°C, preferably comprised between 0° and -90°C.  
15 Such polymers or copolymers may be of natural origin or may be obtained by solution or emulsion polymerization of one or more conjugated diolefins, possibly mixed with one or more monovinylarenes in an amount generally not higher than 50% by weight.

20 Generally, the conjugated diolefins have from 4 to 12, preferably from 4 to 8, carbon atoms, and may be selected from the group comprising: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 3-butyl-1,3-octadiene, 2-phenyl-1,3-butadiene, and the like,  
25 or mixtures thereof. 1,3-butadiene and isoprene are particularly preferred.

Monovinylarenes possibly usable as comonomers  
generally have from 8 to 20, preferably from 8 to 12 carbon  
atoms, and may be selected for instance from: 1-  
30 vinyl naphthalene; 2-vinyl naphthalene; various alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl styrene derivatives, such as for instance: alpha-methylstyrene, 3-methylstyrene, 4-propylstyrene, 4-cyclohexylstyrene, 4-

dodecylstyrene, 2-ethyl-4-benzylstyrene, 4-p-tolylstyrene, 4-(4-phenylbutyl)styrene, and the like, or mixtures thereof. Styrene is particularly preferred.

Preferably, the elastomeric diene polymers usable as a  
5 polymeric base in the present invention may be selected  
from: cis-1,4-polyisoprene (either natural or synthetic,  
preferably natural rubber), 3,4-polyisoprene, poly-1,3-  
butadiene (in particular, high vinyl 1,3-polybutadiene  
having a content of 1,2-polymerized units comprised between  
10 15 and 85% by weight), polychloroprene, possibly  
halogenated isoprene/isobutene copolymers, 1,3-  
butadiene/acrylonitrile copolymers, styrene/1,3-butadiene  
copolymers, 1,3-butadiene/isoprene copolymers, styrene/  
isoprene/1,3-butadiene copolymers, butadiene/acrylonitrile  
15 copolymers, and the like, or mixtures thereof.

Diene polymers functionalized by reaction with  
suitable terminating or coupling agents may also be  
employed. In particular, diene polymers obtained by anionic  
polymerization in the presence of an organometal initiator  
20 (in particular, an organo-lithium initiator) may be  
functionalized by reaction of the organometallic residues  
deriving from the initiator with suitable terminating or  
coupling agents such as imines, carbodiimides, alkyltin  
halides, substituted benzophenones, alkoxy- or aryloxy  
25 silanes (see, for instance, European patent EP-451,604 and  
US patents 4,742,124 and 4,550,142).

At least one reinforcing filler may be advantageously  
added to the compositions according to the present  
invention, in an amount preferably comprised between 0.1  
30 and 120 phr, preferably between 20 and 90 phr (phr = parts  
by weight per 100 parts of polymer base). The reinforcing  
filler may be selected from those commonly employed for  
cross-linked products, and in particular for tires, such  
as: carbon black, silica, alumina, aluminum silicates,

calcium carbonate, kaolin and the like, or mixtures thereof. Carbon black, silica, or mixtures thereof are particularly preferred.

5 The carbon black grades usable according to the present invention may be selected from those conventionally used in tire manufacture, generally having a surface area not smaller than 20 m<sup>2</sup>/g (determined by CTAB absorption as described in ISO standard 6810).

10 The silica usable according to the present invention may generally be pyrogenic silica or, preferably, precipitated silica having a BET surface area comprised between 50 and 500 m<sup>2</sup>/g, preferably between 70 and 200 m<sup>2</sup>/g (measured according to ISO standard 5794/1).

15 If a reinforced filler comprising silica is present, the composition may advantageously incorporate a coupling agent capable of interacting with silica and to bind the latter to the polymer base during vulcanization.

20 Coupling agents of preferred use are those based on silane, identifiable for instance by the following structural formula:



wherein:

groups R, equal or different from each other, are selected from: alkyl, alkoxy, aryloxy groups or halogen atoms, with  
25 the proviso that at least one of the R groups is an alkoxy or aryloxy group;

n is an integer of from 1 to 6;

X is a group selected from: nitrous, mercapto, amino, epoxy, vinyl, imido, chloro,  $-(S)_m-C_nH_{2n}-Si(R)_3$ , wherein m  
30 and n are integers of from 1 to 6, and the R groups are as

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defined above.

Among them, the silane-based coupling agent bis(3-trietoxysilylpropyl)tetrasulfide (Si69) is particularly preferred, either as such or suitably mixed with a small amount of inert filler (for instance, carbon black) to facilitate the incorporation of the same in the rubber composition.

The compositions according to the present invention may be vulcanized according to known techniques, and in particular with sulfur-based vulcanizing systems commonly employed for diene elastomers. To this end, after a first thermal-mechanical working steps, a sulfur-based vulcanizing agent is incorporated in the composition together with vulcanization activators and accelerators. In this second working step, the temperature is generally kept below 120°C, preferably below 100°C, to prevent undesired pre-cross-linking phenomena.

The vulcanizing agent of most advantageous use is sulfur or sulfur-containing molecules (sulfur donors) with accelerators and activators known to anyone skilled in the art.

Particularly effective activating agents are zinc compounds and in particular ZnO, ZnCO<sub>3</sub>, zinc salts of fatty acids, saturated or unsaturated, having from 8 to 18 carbon atoms, such as for instance zinc stearate, preferably formed in situ in the rubber composition starting from ZnO and fatty acid, as well as BiO, PbO, Pb<sub>3</sub>O<sub>4</sub>, PbO<sub>2</sub>, and mixtures thereof.

Accelerators of common use may be selected from: dithiocarbamates, guanidines, thioureas, thiazoles, sulphenamides, tiourams, amines, xanthates, and the like, or mixtures thereof.



The compositions according to the present invention may include other additives of common use selected on the basis of each specific application they are intended for. For instance, the following may be added to said  
5 compositions: antioxidants, antiageing agents, plasticizers, adhesive agents, antiozonants, modifying resins, fibers (for instance, Kevlar® pulp), and the like.

In particular, in order to further improve processability, a lubricant, generally selected from  
10 mineral oils, vegetable oils, synthetic oils and the like, or mixtures thereof, for instance: aromatic oil, naphthene oil, phthalates, soybean oil, and the like, may be added to the cross-linking compositions of the present invention. The amount of the lubricant may generally range between 2  
15 and 100 phr, preferably between 5 and 50 phr.

The preparation of the compositions according to the present invention may be carried out by mixing the polymer components with the possibly present reinforcing filler and the other additives according to techniques known in the  
20 art. Mixing may be carried out for instance by means of an open-mill type mixer, or by means of an internal mixer of the type with tangential (Banbury) or interpenetrating (Intermix) rotors, or in continuous mixers of the Ko-Kneader (Buss) type, or of twin-screw co-rotating or  
25 counter-rotating type.

The hydrophilic polymer and the functionalized polymer may be used in the form of powder, beads or pellets. In order to improve mixing with the other components, such polymers may be used combined with a plasticizer, such as  
30 glycerin, pentaerythrite, and the like. Preferably, the compositions according to the present invention are produced in two steps. In a first step, the mixture of the hydrophilic polymer and of the functionalized polymer is prepared, possibly with a portion of the elastomeric base,

thereby forming a masterbatch. In a subsequent step, the masterbatch is mixed with the remaining portion of the elastomeric base and the other components, according to conventional methods. The first step of masterbatch preparation is preferably carried out in a continuous mixer, for instance a twin-screw extruder, at a temperature of more than 120°C, so as to obtain an excellent dispersion of the thermoplastic polymers in the elastomeric base. The continuous mixers of preferred use are characterized by an adjustable geometry of the screw and thermal profile of the cylinder.

Now, the present invention will be further illustrated by some examples, with reference to:

the attached Figure 1, which shows a partly interrupted view in cross-section of a tire according to the invention.

With reference to Figure 1, a tire 1 conventionally comprises at least one carcass ply 2 whose opposite side edges are externally bent around respective bead wires 3, each incorporated in a bead 4 along a circumferential internal edge of the tire, at which said tire engages on a rim 5 which makes part of a vehicle wheel.

Along the circumferential development of the carcass ply 2 one or more belt strips 6, made of textile or metal chords incorporated in a sheet of rubber composition, are applied. Externally to the carcass ply 2, in respective opposite side portions of the same, a couple of sidewalls 7 is applied, each of which extends from the bead 4 up to a so-called "shoulder" zone 8 of the tire, defined at the opposite ends of the belt strip 6. A tread 9, whose side edges terminate at the shoulders 8, connecting with the side walls 7, is circumferentially applied on the belt strips 6. The tread 9 is externally provided with a rolling

surface 9a, intended for getting in touch with the ground, wherein circumferential grooves 10 may be formed, intercalated with transversal slits, not shown in the attached figure, which define a plurality of blocks 11, variously distributed on said rolling surface 9a.

The production process of the tire according to the present invention may be carried out with techniques and apparatuses known in the art. More particularly, such process comprises an assembling step of the green tire, wherein several semi-finished products, previously and separately prepared from each other and corresponding to the different parts of the tire (carcass plies, belt strips, bead wires, fillings, sidewalls and treads) are associated with each other with a suitable assembling machine.

Afterwards, the green tire thus obtained is transferred to the subsequent shaping and cross-linking steps. To this end, a vulcanization mold is used, adapted to house the tire under working within a molding cavity having walls counter-shaped with respect to the outer surface of the tire once the cross-linking has been completed.

Shaping of the green tire may be carried out by feeding a pressurized fluid into the space defined by the tire inner surface, in order to press the outer surface of the green tire against the walls of the molding cavity. In one of the most widely used shaping methods, a vulcanization chamber made of elastomeric material, filled with vapor and/or other fluids, is inflated within the tire enclosed in the molding cavity. In this way, the green tire is pushed against the inner walls of the molding cavity, obtaining the desired shaping. Alternatively, shaping may be carried out without an inflatable vulcanization chamber, by preparing within the tire a toroidal metal support

shaped in accordance to the configuration of the inner surface of the tire to be obtained (see for instance patent EP-242 840). The different coefficient of thermal expansion between the toroidal metal support and the green elastomeric material is exploited to achieve an adequate molding pressure.

At this point, the cross-linking step of the green elastomeric material present in the tire is carried out. To this aim, the outer wall of the vulcanization mold is caused to get in touch with a heating fluid (generally, vapor), so that the outer wall reaches a maximum temperature generally comprised between 100°C and 230°C. At the same time, the inner surface of the tire is brought to the cross-linking temperature with the same pressurized fluid employed to press the tire against the walls of the molding cavity, heated up to a maximum temperature comprised between 100 and 250°C. The time necessary to obtain a satisfactory degree of cross-linking throughout the mass of the elastomeric material may generally range between 3 min and 90 min, and mainly depends on the tire size.

Some embodiments of the present invention are reported in the following.

EXAMPLES 1-3:

Preparation of a masterbatch comprising the hydrophilic polymer

Compositions according to the present invention (masterbatch) were prepared as shown in Table 1. For comparison, compositions were also prepared which contained the hydrophilic polymer but not the functionalized polymer (Example 2) and compositions which contained the hydrophilic polymer combined with a polymer that had no reactive functional groups (Example 3).

A mixture of the ingredients reported in Table 1 (the amounts are expressed as % by weight of the total) was fed to a parallel twin-screw (co-rotating) extruder having a length/diameter ratio  $L/D = 30$ . The maximum temperature reached during the extrusion was of  $200^{\circ}\text{C} \pm 5^{\circ}\text{C}$ . The masterbatch was air cooled.

The compositions thus obtained were analyzed with an optical microscope in order to evaluate the dispersion of the hydrophilic polymer within the elastomeric matrix, according to the following method.

#### Preparation of samples

A 3 g sample of each composition was pressure-molded in a Prestopress-Struers press (conditioning time: 15 min; pressure = 1 atm; maximum temperature =  $110^{\circ}\text{C}$ ).

From the discs thus obtained, sections having a thickness of  $5\text{ }\mu\text{m}$  were obtained using a Reichert-Jung 2050 microtome equipped with a LN20 cryogenic unit (cutting temperature:  $-70^{\circ}\text{C}$ ). The sections thus obtained were placed on a slide previously cooled at  $-70^{\circ}\text{C}$ .

#### Optical analysis

The sections thus prepared were observed with a transmission optical microscope with polarized light (Polyvar Met model; 10X lenses, multiplication factor = 1, equipped with polarizer and analyzer). Twenty images for each sample were memorized through a JVC TK1280E videocamera with a Y/C connecting cable. The images were computer-analyzed (by means of an Image Pro Plus - Media Cybernetic software), measuring for the particles having a clear color, corresponding to domains containing the hydrophilic polymer, the mean area and mean diameter values, and the mean number of particles per surface unit of the sample. The results are reported in Table 1.

TABLE 1

Example	1	2 (*)	3 *
SBR	75	75	75
PVA	19	25	19
PE-MA	6	--	--
PEB	--	--	6
Microscope analysis			
Average area ( $\mu\text{m}^2$ )	145.94	323.12	220.10
No. of particles ( $\text{mm}^{-2}$ )	1786.90	689.50	1121.23
Average diameter ( $\mu\text{m}$ )	11.98	14.10	12.71

(\*) comparative

- 5 SBR: styrene/butadiene copolymer, obtained by emulsion polymerization, containing 40% by weight of styrene, mixed with 37.5 phr of oil (marketed by Enichem Elastomeri under the abbreviation SBR 1721);
- 10 PVA: vinylalcohol/vinylacetate copolymer, obtained by hydrolysis of polyvinylacetate, having a hydrolysis degree of 83 mol %, a viscosity (DIN 53 015) of  $2.8 \pm 0.3 \text{ mPa}\cdot\text{s}^2$  (marketed by Clariant Italia under the trademark Mowiol® 3-83);
- 15 PE-MA: polyethylene grafted with 0.5% by weight of maleic anhydride, having a Melt Flow Index (at  $190^\circ\text{C}$  and 2.16 kg) of 4 (marketed by Elf Atochem under the trademark Orevac® OE 330);

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PEB: ethylene/butene copolymer, having a Melt Flow Index (at 190°C and 2.16 kg) of 3 (marketed by Exxon under the trademark Escorene® LL 1004).

EXAMPLES 4-6 (silica-containing rubber compositions)

5 Sulfur-vulcanizable silica-containing rubber compositions were prepared. The compositions are reported in Table 2A (in phr). With respect to the reference rubber composition containing 70 phr of silica (Example 4), the rubber compositions of Examples 5-6 contain 6.3 phr of PVA  
10 according to the invention (Example 5) or 6.3 phr of starch/PVA composite according to US patent 5,672,639 (Example 6) instead of 10 phr of silica. The amounts expressed in phr of silica and of hydrophilic polymers are not equal, since, as known, to evaluate the reinforcing  
15 properties of a filler, reference must be made to the parts by volume and not to the parts by weight.

All the ingredients, except for sulfur and the accelerators were mixed in an internal mixer (model Pomini PL 1.6) for about 5 min (1<sup>st</sup> step). As soon as the  
20 temperature of 145 ± 5°C was reached, the rubber composition was discharged. Thereafter, sulfur and the accelerating agents were added by mixing in a laboratory cylinder open mixer (2<sup>nd</sup> step).

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TABLE 2A

Example	4 (*)	5	6 (*)
1 <sup>st</sup> step			
SBR	84	65,3	84
BR	39	39	39
SiO <sub>2</sub>	70	60	60
Masterbatch (Ex. 1)	--	25	--
Starch/PVA	--	--	6.3
Silane	5.6	5.6	5.6
Stearic acid	2	2	2
ZnO	2.5	2.5	2.5
Aromatic oil	5	5	5
Antioxidant	2	2	2
Microcrystalline wax	1	1	1
2 <sup>nd</sup> step			
Sulfur	1.4	1.4	1.4
DPG	1.9	1.9	1.9
CBS	1.8	1.8	1.8

(\*) comparative

SBR: styrene/butadiene copolymer, obtained by emulsion polymerization, containing 25% by weight of styrene, mixed with 37.5 phr of oil (marketed by Bayer under the abbreviation SBR 5025);

BR: cis-1,4-polybutadiene (product Europrene Neocis® BR 40 - Enichem Elastomeri);

DPG: diphenyl guanidine (product Vulkacit® D - Bayer);

10 CBS: N-cyclohexyl-2-benzothiazyl-sulfenamide (product

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Vulkacit® CZ - Bayer);

SiO<sub>2</sub>: precipitated silica (product Zeosil® 1165 MP - Rhône-Poulenc);

5 Starch/PVA: composite of destructured starch and ethylene/vinylalcohol copolymer in a 1.5/1 weight ratio, having a softening point of 147°C (ASTM D1228), the starch having an amylose/amylopectine weight ratio of about 1/3, a humidity content of about 5% by weight (product Mater Bi® 1128R - Novamont);

10 Silane: bis(3-triethoxysilylpropyl)tetrasulfide (product X50S comprising 50% carbon black and 50% silane - Degussa) (the amounts reported in the table refer to silane only);

Antioxidant: phenyl-p-phenylene diamine.

15 The compositions thus prepared were submitted to MDR rheometric analysis utilizing a Monsanto MDR rheometer, carrying out the tests at 151°C for 60 min with an oscillation frequency of 1.66 Hz (100 oscillations per minute) and an oscillation amplitude of ±0.5°. The  
20 mechanical properties (according to ISO standard 37) and the hardness in IRHD degrees at 23°C and 100°C (according to ISO standard 48) were measured on samples of the aforesaid compositions cross-linked at 151°C for 30 minutes. The results are shown in Table 2B.

25 Table 2B also shows the dynamic elastic properties, measured with a dynamic Instron device in the traction-compression mode according to the following method. A test piece of the cross-linked material having a cylindrical form (length = 25 mm; diameter = 14 mm), compression-  
30 preloaded up to a 10% longitudinal deformation with respect to the initial length, and kept at the prefixed temperature (70°C or 10°C) for the whole duration of the test, was

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submitted to a dynamic sinusoidal strain having an amplitude of  $\pm 3.33\%$  with respect to the length under pre-load, with a 100 Hz frequency. The dynamic elastic properties are expressed in terms of dynamic elastic modulus ( $E'$ ) and tandelta (loss factor) values. As is known, the tandelta value is calculated as a ratio between the viscous modulus ( $E''$ ) and the elastic modulus ( $E'$ ), both of them being determined with the above dynamic measurements.

10        Lastly the DIN abrasion values were measured according to ISO standard 4649, also reported in Table 2B, expressed as relative volumetric loss with respect to the reference composition of Example 4 (assumed to be 100).

TABLE 2B

Example	4 (*)	5	6 (*)
Rheometric properties			
Max torque (dN·m)	23.1	22.2	21.8
Min. torque (dN·m)	3.0	2.3	2.7
Delta torque (dN·m)	20.1	19.9	19.1
t <sub>90</sub> (min)	21.0	20.0	30.0
Mechanical properties			
100% Modulus (MPa)	2.50	2.70	3.07
300% Modulus (MPa)	9.59	9.55	10.05
Stress at break (MPa)	16.20	15.30	13.80
Elongation at break (%)	485	435	395
300% Mod./100% Mod.	3.8	3.5	3.3
Dynamic properties			
E' (70°C) (MPa)	6.20	6.39	6.25
E' (10°C) (MPa)	8.42	9.46	8.51
Tandelta (70°C)	0.112	0.095	0.093
Tandelta (10°C)	0.270	0.254	0.238
IRHD hardness at 23°C	74	73	74
IRHD hardness at 100°C	69	68	69
DIN abrasion	100	105	125

(\*) comparative

EXAMPLES 7-9 (rubber compositions containing carbon black)

- 5 Sulfur-vulcanizable rubber compositions containing carbon black were prepared with the same method described

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for Examples 4-6. The compositions thus obtained are reported in Table 3A (in phr). With respect to the reference rubber composition containing 70 phr of carbon black (Ex. 7), the rubber compositions of Examples 8-9 contain 7 phr of PVA according to the invention (Ex. 8) or 7 phr of starch/PVA composite according to US patent 5,672,639 (Ex. 9), instead of 10 phr of carbon black.

The same measurements of Examples 4-6 were carried out on the rubber compositions thus obtained. The results are shown in Table 3B.

TABLE 3A

Example	7 (*)	8	9 (*)
1 <sup>st</sup> step			
SBR	84	63	84
BR	39	39	39
C.B.	70	60	60
Masterbatch (Ex. 1)	--	26	--
Starch/PVA	--	--	7
Silane	--	0.7	0.7
Stearic acid	2	2	2
ZnO	2.5	2.5	2.5
Aromatic oil	5	5	5
Antioxidant	2	2	2
Microcrystalline wax	1	1	1
2 <sup>nd</sup> step			
Sulfur	1.4	1.4	1.4
DPG	1.9	1.9	1.9
CBS	1.6	1.6	1.8

(\*) comparative

SBR: styrene/butadiene copolymer, obtained by emulsion polymerization, containing 25% by weight of styrene, mixed with 37.5 phr of oil (marketed by Bayer under the abbreviation SBR 5025);

BR: cis-1,4-polybutadiene (product Europrene Neocis® BR 40 - Enichem Elastomeri);

DPG: diphenyl guanidine (product Vulkacit® D - Bayer);

10 CBS: N-cyclohexyl-2-benzothiazyl-sulfenamide (product

Vulkacit® CZ - Bayer);

C.B.: N234 carbon black (Cabot);

5 Starch/PVA: composite of destructured starch and ethylene/vinylalcohol copolymer in a 1.5/1 weight ratio, having a softening point of 147°C (ASTM D1228), the starch having an amylose/amylopectine weight ratio of about 1/3, a humidity content of about 5% by weight (product Mater Bi® 1128R - Novamont);

10 Silane: bis(3-triethoxysilylpropyl)tetrasulfide (product X50S comprising 50% carbon black and 50% silane - Degussa) (the amounts reported in the table refer to silane only);

Antioxidant: phenyl-p-phenylene diamine.

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TABLE 3B

Example	7 (*)	8	9 (*)
Rheometric properties			
Max torque (dN·m)	21.2	18.7	17.8
Min. torque (dN·m)	4.4	3.4	3.6
Delta torque (dN·m)	16.6	15.3	14.2
t <sub>90</sub> (min)	13.3	11.9	11.8
Mechanical properties			
100% Modulus (MPa)	3.17	3.10	2.85
300% Modulus (MPa)	13.30	12.10	11.00
Stress at break (MPa)	15.80	15.10	13.32
Elongation at break (%)	380	403	375
300% Mod./100% Mod.	4.2	3.9	3.9
Dynamic properties			
E' (70°C) (MPa)	7.51	6.78	6.31
E' (10°C) (MPa)	12.83	11.72	11.10
Tandelta (70°C)	0.191	0.173	0.170
Tandelta (10°C)	0.337	0.316	0.320
IRHD hardness at 23°C	75	74	72
IRHD hardness at 100°C	70	67	66
DIN abrasion	100	115	130

(\*) comparative

EXAMPLES 10-11 (rubber compositions containing silica and carbon black)

- 5 Sulfur-vulcanizable rubber compositions containing silica and carbon black were prepared with the same method

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described for Examples 4-6. The compositions are reported in Table 4A (in phr).

The same measurements of Examples 4-6 were carried out on the rubber compositions thus obtained.

5        Additionally, the water absorption capacity of the prepared rubber compositions was also evaluated with the following method.

10        A sample of rubber composition was vulcanized in a press heated to 151°C for 30 min. Polytetrafluoroethylene sheets were interposed between the rubber composition and the press platens to prevent any contamination and adhesion of said rubber composition. Sheets measuring 120 x 120 mm and having a thickness of about 1.0 mm were obtained in this way. Rectangular samples measuring 60 x 30 mm were cut  
15        from these sheets. Said samples were oven-dried at 65°C for 48 hours and then exposed to dry air in a dry-box at room temperature for 48 hours. The weight of the samples so dried was registered. The samples were then immersed in  
20        water at two different temperatures (4°C and 23°C) and their weight was measured after 28, 51 and 118 hours of immersion. Table 4C shows the results obtained, expressed as percent variation of the weight based on the starting weight.

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TABLE 4A

Example	10 (*)	11
1 <sup>st</sup> step		
SBR	75	53
BR	25	25
SiO <sub>2</sub>	35	35
C.B.	35	25
Masterbatch (Ex. 1)	--	29
Silane	3.5	3.5
Stearic acid	2	2
ZnO	3	3
Aromatic oil	15	15
Antioxidant	2	2
Microcristalline wax	1	1
2 <sup>nd</sup> step		
Sulfur	1.2	1.2
CBS	2.5	2.5

(\*) comparative

SBR: styrene/butadiene copolymer, obtained by emulsion polymerization, containing 40% by weight of styrene, mixed with 37.5 phr of oil (marketed by Enichem Elastomeri under the abbreviation SBR 1721);

BR: cis-1,4-polybutadiene (product Europrene Neocis® BR 40 - Enichem Elastomeri);

DPG: diphenyl guanidine (product Vulkacit® D - Bayer);

10 CBS: N-cyclohexyl-2-benzothiazyl-sulfenamide (product Vulkacit® CZ - Bayer);

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SiO<sub>2</sub>: precipitated silica (product Zeosil® 1165 MP - Rhône-Poulenc);

C.B.: N234 carbon black (Cabot);

5 Starch/PVA: composite of destructured starch and ethylene/vinylalcohol copolymer in a 1.5/1 weight ratio, having a softening point of 147°C (ASTM D1228), the starch having an amylose/amylopectine weight ratio of about 1/3, a humidity content of about 5% by weight (product Mater Bi® 1128R - Novamont);

10 Silane: bis(3-triethoxysilylpropyl)tetrasulfide (product X50S comprising 50% carbon black and 50% silane - Degussa) (the amounts reported in the table refer to silane only);

Antioxidant: phenyl-p-phenylene diamine.

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TABLE 4B

Example	10 (*)	11
Max torque (dN·m)	15.5	16.4
Min. torque (dN·m)	3.1	2.6
Delta torque (dN·m)	13.4	13.8
t90 (min)	15.0	15.0
100% Modulus (MPa)	2.5	2.6
300% Modulus (MPa)	11.0	11.2
Stress at break (MPa)	17.3	16.4
Elongation at break (%)	474	456
300% Mod./100% Mod.	4.4	4.3
E' (70°C) (MPa)	6.1	6.0
E' (10°C) (MPa)	14.9	15.5
Tandelta (70°C)	0.230	0.200
Tandelta (10°C)	0.609	0.569
IRHD hardness at 23°C	75	74
IRHD hardness at 100°C	63	62
DIN abrasion	100	102

(\*) comparative

TABLE 4C

Example	10 (*)	11
Immersion in water at 23°C		
28 hours	1.1	1.7
51 hours	1.7	2.3
118 hours	2.3	3.2
Immersion in water at 4°C		
28 hours	0.8	1.0
51 hours	1.1	1.3
118 hours	1.4	1.8

(\*) comparative

\* \* \* \* \*

From the experimental results reported above, the  
5 following may be noticed.

The presence of the functionalized polymer ensures an excellent dispersion of the hydrophilic polymer throughout the polymer matrix, as proved by optical analysis (Ex. 1-3, Tab. 1).

10 In the rubber compositions containing silica as a reinforcing filler, the partial replacement of silica with a combination of hydrophilic polymer and functionalized polymer according to the present invention allows to  
15 achieve, with respect to similar compositions wherein a destructured starch/PVA composite is employed, a more marked reinforcing effect, as evidenced by the high modulus values, in particular at high elongation, 300% modulus/100% modulus ratio and stress at break. The cross-linked product also shows improved hysteretic properties, in particular

higher tandelta values at 10°C with the same values of tandelta at 70°C (i.e. a better road grip on wet grounds with the same rolling resistance). These effects have been achieved without significantly worsening abrasion resistance.

The reinforcing effect of the hydrophilic polymer according to the present invention remains in any event high also when the hydrophilic polymer partly replaces carbon black, which, as known, is a particularly effective reinforcing filler. This is proved by the mechanical properties (modulus, elongation and stress at break) and by the abrasion resistance, which maintains with values comparable to those of the compositions only containing carbon black. The same effect is obtained by employing the destructured starch/PVA composite (see Examples 7-9, Tables 3A-3B).

The same behavior is achieved with rubber compositions reinforced with mixtures of silica and carbon black (see Examples 10-11, Tables 4A-4B).

Without being bound in any way to any interpretative theory, the Applicant believes that the improved reinforcing capabilities of the hydrophilic polymer combined with the functionalized polymer according to the present invention with respect to the plasticized destructured starch are due to an improved interaction of the hydrophilic polymer with the elastomeric matrix and with the reinforcing filler, if present. Conversely, destructured starch tends to favor intramolecular interaction to the detriment of interactions with the elastomeric matrix and with the reinforcing filler, so that it turns out to be poorly compatibilized within the cross-linked material.

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## CLAIMS

1. A tire for vehicle wheels comprising at least one element made of an elastomeric material, characterized in that said element includes a composition comprising:

- 5       (a) at least one elastomeric diene polymer;  
      (b) at least one thermoplastic polymer having a main hydrocarbon chain to which hydrophilic groups are linked;  
      (c) at least one polymer containing functional groups reactive with said hydrophilic groups.

10       2. The tire according to claim 1, wherein said element including said composition is a tread belt.

3. The tire according to anyone of the preceding claims, wherein the hydrophilic polymer is present in the composition in an amount comprised between 0.1 and 100 phr.

15       4. The tire according to anyone of the preceding claims, wherein the functionalized polymer is present in the composition in an amount so as to obtain a weight ratio between the hydrophilic polymer and the functionalized polymer comprised between 0.5:1 and 10:1.

20       5. The tire according to anyone of the preceding claims, wherein the hydrophilic polymer comprises hydrophilic groups selected from:

- hydroxyl groups -OH;  
      carboxylic groups -COOH, possibly at least partially  
25   in the salt form;  
      ester groups -COOR (R = alkyl or hydroxyalkyl);  
      amide groups -CONH<sub>2</sub>;  
      sulfonic groups -SO<sub>3</sub>H, possibly at least partially in the salt form.

30       6. The tire according to anyone of the preceding claims, wherein the hydrophilic polymer is capable of absorbing at least 0.1% by weight of water based on the

polymer weight after a 24-hour exposure in an environment having a 50% relative humidity at the temperature of 24°C (according to ASTM standard D570).

7. The tire according to anyone of the preceding claims, wherein the hydrophilic polymer has a melting temperature lower than 230°C.

8. The tire according to anyone of the preceding claims, wherein the hydrophilic polymer is selected from: polyacrylic acid, polymethacrylic acid, polyhydroxy-alkylacrylate, polyalkylacrylate, polyacrylamide, acrylamide/acrylic acid copolymers, polyvinylalcohol, polyvinylacetate, vinylalcohol/vinylacetate copolymers, ethylene/vinylacetate copolymers, ethylene/vinylalcohol copolymers, ethylene/vinylalcohol/vinylacetate terpolymers, polyvinylsulfonic acid, polystyrene sulfonate, and mixtures thereof.

9. The tire according to anyone of the preceding claims, wherein the hydrophilic polymer comprises repeating units having the formula:



with a random or block distribution along the chain.

10. The tire according to claim 9, wherein the hydrophilic polymer is selected from:

(i) vinylalcohol polymers obtained by hydrolysis of polyvinylacetate, with a hydrolysis degree comprised between 50 and 100 mol %;

(ii) ethylene/vinylalcohol copolymers having a content of ethylene units comprised between 20 and 60 mol %.

11. The tire according to anyone of the preceding

claims, wherein the functionalized polymer is a thermoplastic hydrocarbon polymer having functional groups selected from: carboxylic groups, anhydride groups, ester groups, silane groups, epoxy groups.

5        12. The tire according to anyone of the preceding claims, wherein the functionalized polymer has an amount of functional groups comprised between 0.05 and 50 parts by weight, based on 100 parts by weight of the polymer.

10        13. The tire according to anyone of the preceding claims, wherein the composition comprising the hydrophilic polymer further includes at least one reinforcing filler.

14. The tire according to claim 13, wherein the reinforcing filler is carbon black.

15        15. The tire according to claim 13, wherein the reinforcing filler is silica.

16. The tire according to claim 13, wherein the reinforcing filler is a mixture of carbon black and silica.

20        17. The tire according to claim 15 or 16, wherein the composition comprising the hydrophilic polymer further includes a silica coupling agent.

18. The tire according to anyone of the preceding claims, wherein the composition comprising the hydrophilic polymer is cross-linked by means of a sulfur-based vulcanizing agent.

25        19. An elastomeric composition comprising:

- (a) at least one elastomeric diene polymer;
  - (b) at least one thermoplastic polymer having a main hydrocarbon chain to which hydrophilic groups are linked;
  - (c) at least one polymer containing functional groups
- 30        reactive with said hydrophilic groups.



20. The composition according to claim 19, wherein the hydrophilic polymer is present in an amount comprised between 0.1 and 100 phr.

5 21. The composition according to anyone of claims from 19 to 20, wherein the functionalized polymer is included in an amount so as to obtain a weight ratio between the hydrophilic polymer and the functionalized polymer comprised between 0.5:1 and 10:1.

10 22. The composition according to anyone of claims from 19 to 21, wherein the hydrophilic polymer comprises hydrophilic groups selected from:

hydroxyl groups -OH;  
carboxylic groups -COOH, possibly at least partially in the salt form;  
15 ester groups -COOR (R = alkyl or hydroxyalkyl);  
amide groups -CONH<sub>2</sub>;  
sulfonic groups -SO<sub>3</sub>H, possibly at least partially in the salt form.

20 23. The composition according to anyone of claims from 19 to 22, wherein the hydrophilic polymer is capable of absorbing at least 0.1% of water based on the polymer weight, after a 24-hour exposure in an environment having a 50% relative humidity at the temperature of 24°C (according to ASTM standard D570).

25 24. The composition according to anyone of claims from 19 to 23, wherein the hydrophilic polymer has a melting temperature lower than 230°C.

25. The composition according to anyone of claims from 19 to 24, wherein the hydrophilic polymer is selected from:  
30 polyacrylic acid, polymethacrylic acid, polyhydroxyalkylacrylate, polyalkylacrylate, polyacrylamide, acrylamide/acrylic acid copolymers, polyvinylalcohol, polyvinylacetate, vinylalcohol/vinylacetate copolymers,

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ethylene/vinylacetate copolymers, ethylene/vinylalcohol copolymers, ethylene/vinylalcohol/vinylacetate terpolymers, polyvinylsulfonic acid, polystyrene sulfonate, and mixtures thereof.

- 5           26. The composition according to anyone of claims from 19 to 25, wherein the hydrophilic polymer comprises repeating units having the formula:



with a random or block distribution along the chain.

- 10           27. The composition according to claim 26, wherein the hydrophilic polymer is selected from:

- (i) vinylalcohol polymers obtained by hydrolysis of polyvinyl acetate, with a hydrolysis degree comprised between 50 and 100 mol %;
- 15           (ii) ethylene/vinylalcohol copolymers having a content of ethylene units comprised between 20 and 60 mol %.

28. The composition according to anyone of claims from 19 to 27, wherein the functionalized polymer is a thermoplastic hydrocarbon polymer having functional groups selected from: carboxylic groups, anhydride groups, ester groups, silane groups, epoxy groups.
- 20

29. The composition according to anyone of claims from 19 to 28, wherein the functionalized polymer has an amount of functional groups comprised between 0.05 and 50 parts by weight, based on 100 parts by weight of polymer.
- 25

30. The composition according to anyone of claims from 19 to 29, comprising at least one reinforcing filler.

31. The composition according to claim 30, wherein the reinforcing filler is carbon black.

32. The composition according to claim 30, wherein the reinforcing filler is silica.

33. The composition according to claim 30, wherein the reinforcing filler is a mixture of carbon black and silica.

5        34. The composition according to claim 32 or 33, further comprising a silica coupling agent.

35. The composition according to anyone of claims from 9 to 34, further comprising a sulfur-based vulcanizing agent.

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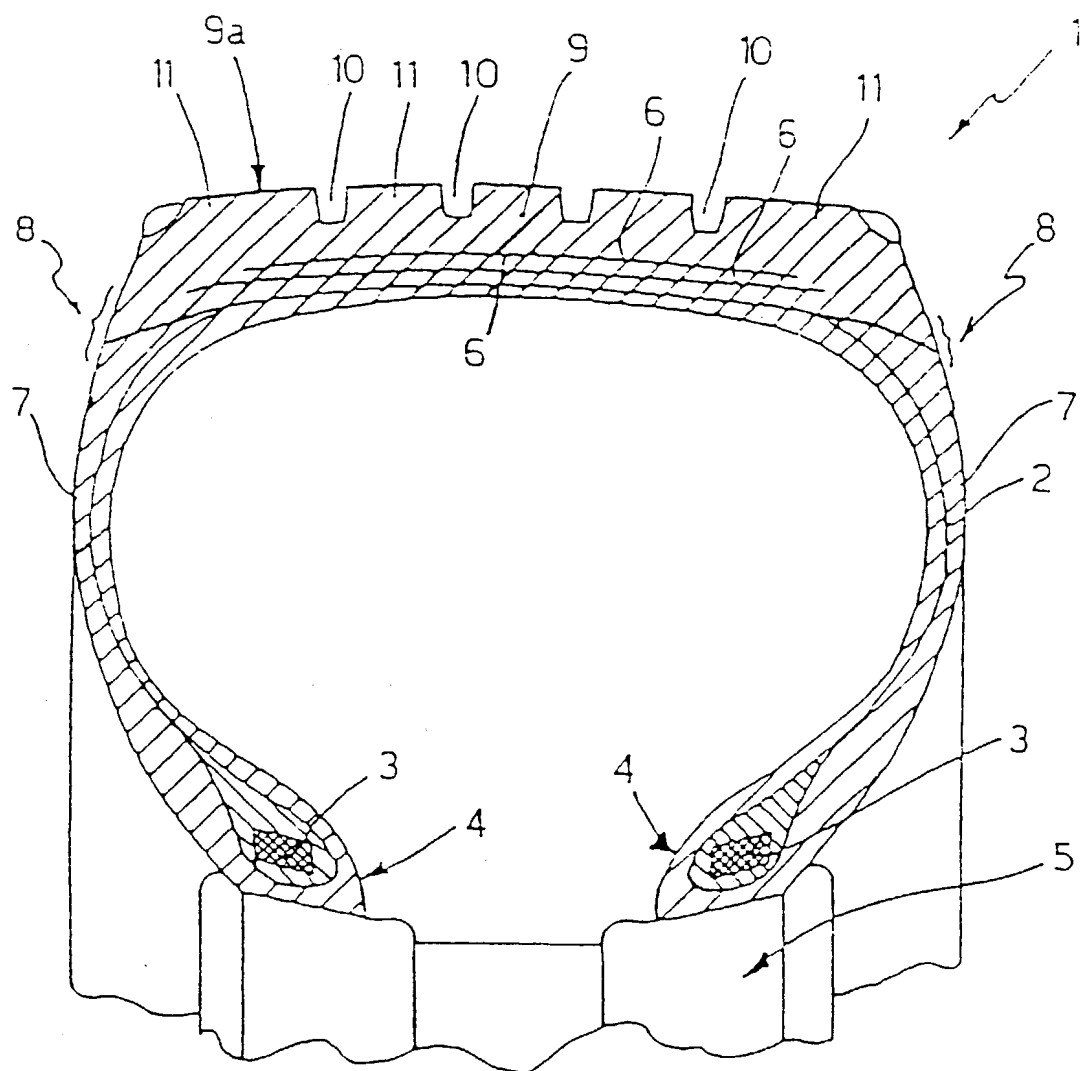


Fig. 1

# INTERNATIONAL SEARCH REPORT

Internat. Application No

PCT/EP 00/12856

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08L21/00 B60C1/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L B60C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	GB 992 016 A (POLYPLASTIC) 12 May 1965 (1965-05-12) claims; example 3 ---	19-35
X	US 3 856 723 A (MACHURAT J ET AL) 24 December 1974 (1974-12-24) abstract; claims; examples ---	19-27, 30-35
A	EP 0 795 581 A (GOODYEAR TIRE & RUBBER) 17 September 1997 (1997-09-17) cited in the application abstract; claims; examples -----	1-35

☐ Further documents are listed in the continuation of box C

☒ Patent family members are listed in annex

**Special Categories of cited documents**

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*I\* earlier document but published on or after the international filing date

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